KINETIC COEFFICIENTS OF SUBSTRATE UTILIZATION AND BIOMASS GROWTH IN THE BIO-DEGRADATION OF PETROLEUM REFINERY WASTEWATER IN AN ACTIVATED SLUDGE PROCESS

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ABSTRACT

A study of the kinetics of petroleum refinery wastewater biodegradation in an activated sludge process was carried out in a 25 L bio-reactor, for a time range of 2-10 hours hydraulic retention. Substrate utilization and microbial growth rate were monitored at various hydraulic retention time which shows corresponding increase in microbial growth and coliform count with substrate utilization. Analysis of the results obtained using the Monod and the modified Monod kinetic model gave the following kinetic parameters: Maximum Substrate Utilization Rate= 4.4 day⁻¹, Half Saturation Constant=275 mg/L, Yield Coefficient=0.5083 mgVSS/mgBOD and Endogenous Decay Constant=0.003 day⁻¹.

1. INTRODUCTION

The ever-increasing world population and industrial development have led to the introduction of different types of chemical substances to the environment, leading to considerable deterioration in environmental quality (Taghreed and Muftah, 2018). Petroleum refinery generates enormous wastewater that requires effective treatment before discharge into the environment. A typical petroleum refinery generates wastewater 0.4-1.6 times the volume of crude oil processed (Coelho et al., 2006) which is potentially harmful to man and the environment if not well treated before discharge. According to Qin et al. (2007) biological treatment of petroleum refinery wastewater by an activated sludge process is viable, as it is generally the most economical method for reducing both wastewater toxicity and dissolved organic constituents, although the process is faced with challenges in terms of performance. Earlier, activated sludge process designs were not based on kinetic data but recently, a more rational solution for the design of activated sludge process has been under studies. Process modeling of the activated sludge process as it is currently conceived requires experimental assessment of kinetic and stoichiometry coefficients, these coefficients vary for different wastewater (Tchobanoglous et al., 2003).

Previously Ambreen et al. (2013) used a laboratory-scale reactor to obtain the following kinetic coefficients for diary wastewater: maximum specific growth rate (µ_max) =4.46 day⁻¹, saturation constant (K_s) =534 mg/L, yield coefficient (Y) =0.714 mgVSS/mgCOD and decay coefficient (K_d) =0.038. Similarly Haydar and Aziz (2009) used a laboratory scale completely mixed continuous flow reactor to generate the following kinetic data for tannery wastewater: maximum substrate utilization rate, half velocity constant, cell yield coefficient and decay coefficient of 3.125 day⁻¹, 488 mg/L, 0.64 and 0.035 day⁻¹, respectively.

For petroleum refinery wastewater, Carlos et al. (2013) reported rate constant (k) values of 0.055 and 0.059 L mg⁻¹ VSS day⁻¹, with and without biomass recirculation, respectively for the removal of organic matter in petroleum refinery wastewater treatment in activated sludge process (ASP). Fazel (2016) treated a simulated petroleum refinery wastewater in an aerobic filter bioreactor integrated with a UV reactor and obtained saturation constant (K_s) and maximum utilization rate (U_max) of 110.67 g/Lday and 90.90 g/Lday respectively.

In the present work actual petroleum refinery wastewater was treated in ASP to obtain maximum substrate utilization rate, half saturation constant, yield coefficient and Endogenous decay constant. The determinations of these kinetic parameters are helpful in understanding the kinetics of substrate utilization, sludge production and design of activated sludge process for wastewater treatment (Haydar and Aziz, 2009).

Mechanism and Kinetics of Activated Sludge Process

The mechanism of the activated sludge process is such that microorganism takes in oxygen and feed on the organic materials in the wastewater which enables reproduction of more microorganisms. According to Tchobanoglous et al. (2003), reaction (1), (2) and (3) represent the biochemical reaction in the activated
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sludge process which involves bacterial cell respiration and synthesis using organic pollutants as substrate. Reaction (3), the endogenous respiration stage is the last phase in the process; it takes place when new cells begin to consume their own cell tissue to obtain energy for their cells maintenance and simultaneously release carbon dioxide and water.

Oxidation (Catabolism)

Organics + O₂ → CO₂ + H₂O + Energy (1)

Synthesis (Anabolism)

Organics + O₂ + Nutrients → New Cells + H₂O + CO₂ (2)

Endogenous Respiration (Endogenous metabolism)

Cell matter + O₂ → CO₂ + H₂O + Nutrient + Energy (3)

Generally substrate utilization and cell growth rate in an activated sludge process can be related as described by Sperling (2007) in Equations 4 to 16.

\[ r_{su} = \frac{kSX}{K_s + S} \] (4)

Where \( r_{su} \) = rate of substrate concentration change due to utilization, \( S \) = substrate concentration, \( k \) = maximum specific substrate utilization rate, \( X \) = biomass (microorganism) concentration, \( K_s \) = half saturation coefficient.

The bacteria growth rate is dependent on the rate at which the substrate is utilized; making the bacterial growth rate maximum at maximum substrate utilization rate as shown in Equation 5.

\[ u_{max} = kY \] (5)

Where, \( u_{max} \) = maximum specific growth rate, \( Y \) is the yield coefficient. Therefore,

\[ k = \frac{u_{max}}{Y} \] (6)

The rate of substrate utilization can be further expressed as:

\[ r_{su} = \frac{u_{max}SX}{Y(K_s + S)} \] (7)

The specific growth rate is related to substrate utilization rate as follows:

\[ \mu = \frac{Yr_{su}}{X} \] (8)

Therefore, \( \mu = \frac{u_{max}S}{Y(K_s + S)} \) (9)

Equation (9) is the Monod kinetic model which relates the microbial growth with the substrate concentration. Considering microbial death rate, \( r_d \).

\[ r_d = -(k_d)(X) \] (10)

Where \( k_d \) = endogenous decay coefficient, the endogenous decay coefficient accounts for the loss in cell mass. Growth rate of biomass is proportional to the substrate utilization rate by the synthesis yield coefficient, and biomass decay is proportional biomass present (Sperling, 2007).

Net rate of growth can be obtained as follows:

\[ r_g = -(Y)(r_{su}) - (k_d)(X) \] (11)

Therefore equation (9) becomes:

\[ r_g = \frac{(u_{max})(S)(X)}{K_s} - (K_d)(X) \] (12)

Or as \( r_g = \frac{YkSX}{K_s + S} - K_dX \) (13)

Specific biomass growth rate, \( \mu = \frac{r_g}{X} \) (14)

The corresponding expression for the net specific growth rate is written as:

\[ \mu = \frac{u_{max}S}{Y(K_s + S)} - (K_d) \] (15)

Or in terms of \( Y \) as

\[ \mu = Y \frac{kS}{K_s + S} - K_d \] (16)

Equation (4), (9), (10) and (15) are useful equations to obtain the following kinetic coefficients data: \( k, K_s, K_d \) and \( Y \), which can be used in the prediction of the rate of substrate utilizations and biomass growth rate in an activated sludge process (Haydar and Aziz, 2009).

Understanding of the dynamic nature of substrate utilization and microbial growth rate in ASP is essential, as it can be used as diagnostics tool to improve process performance.

2. METHODOLOGY

Petroleum refinery wastewater sample was collected from the wastewater treatment plant of Kaduna Refining and Petrochemical Company (KRPC) Kaduna. The study was carried out in a 25 L activated sludge process reactor shown in Figure 1. The reactor was seeded with 2 L sludge obtained from the bio-filter unit of KRPC wastewater treatment plant. An air compressor was used to supply air at a rate of 10 L/min into the reactor for aeration and to maintain intimate contact between the influent wastewater and the microbes.

The process was operated at a hydraulic retention time (HRT) of 2, 4, 6, 8 and 10 hrs, at the end of each HRT, effluent was taken for BOD, biomass growth and coliform count analysis using the America Public Health Association (APHA) Standard Method for the Examination of Water (APHA, 2017).
Equation (4) and (16) were linearized to obtain Equation (17) and (18) as shown in Table 1, which were plotted to arrive at the kinetic coefficients (Haydar and Aziz (2009) and Ambreen et al. (2013)).

\[
\frac{X\theta}{S_o - S} = \frac{K_s}{K} \frac{1}{S} + \frac{1}{k} \tag{17}
\]

\[
\frac{1}{\theta} = \frac{S_o - S}{X\theta} Y - K_d \tag{18}
\]

Table 1: Monod and modified Monod Kinetics

<table>
<thead>
<tr>
<th>S/N</th>
<th>Rate Expression</th>
<th>Kinetics</th>
<th>Integrated Form</th>
<th>Plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\frac{ds}{dt} = \frac{KsX}{(Ks + S)})</td>
<td>Monod Kinetics</td>
<td>(\frac{X\theta}{S_o - S} = \frac{Ks}{K} \frac{1}{S} + \frac{1}{k})</td>
<td>Plot of (\frac{X\theta}{S_o - S}) versus (\frac{1}{S})</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{dX}{dt} = Y \frac{dS}{dt} - K_d X)</td>
<td>Modified Monod</td>
<td>(\frac{1}{\theta} = \frac{S_o - S}{X\theta} Y - k_d)</td>
<td>Plot of (\frac{1}{\theta}) versus (\frac{S_o - S}{X\theta})</td>
</tr>
</tbody>
</table>

Where \(X\) is mass of microorganisms, \(S\) is mass of organic matter used as food by the microorganisms (BOD), and \(Y\) is the cell yield coefficient, which is the ratio of the mass of cells formed to the mass of substrate consumed. \(K_d\) represents the proportion of the total mass of microorganisms that self-degrades (endogenous respiration) per unit time, \(K\) is the maximum rate of substrate utilization per unit mass of microorganisms, and \(K_s\) is the half saturation constant, which is the substrate concentration at one half of the maximum growth rate, mass per unit volume.

3. RESULTS AND DISCUSSION

3.1 Cell growth and substrate utilizations

Figure 2 shows that cell growth rate is proportional to the cell concentration \(X\) with gradual utilization of the substrate. Bacteria growth count also shows in Figure 2 that there is a steady increase in bacteria growth from \(1.1 \times 10^5\) to \(6.4 \times 10^5\) cfu after 10 hours of aeration.
Figure 2: Cell Growth and Substrate Utilization

Figure 3 is the Food-Microorganism Ratio (F/M) obtained at various HRT; this indicates how much food is available at a particular time for microorganism to consume. An appropriate F/M ratio is necessary to obtain proper performance from the activated sludge process.

The highest value of 9.0 was obtained at the start of the process when the food (BOD) was very high but it gradually reduces as treatment progresses and more food has been used up for metabolism by the microorganism.

3.2 Determination of bio-kinetic coefficients

Figure 4 and 5 is the plots of the linearized Monod and modified Monod equations in Table 1 which were used to determine the bio-kinetic coefficients for petroleum refinery wastewater bio-degradation in the activated sludge process. Using the Line-Weaver approach, a linear regression line is fitted to the plotted data. The intercept on the y-axis and the slope of this line is used to find $K$ and $K_s$. From the linearized Equation 17 and Figure 4, $K = 4.4 \text{ day}^{-1}$, $K_s = 275 \text{ mg/L}$. 

**Figure 3: Food-to-Micro-organism ratio**
Figure 5 is the plot of the linearized form of the modified Monod equation which was used to obtain $K_d$ and $Y$. A plot of $1/\theta$ against $(S_0-S)/X\theta$ gives an intercept which represents $K_d$, while the slope represents $Y$. Therefore, an Endogenous Decay Constant ($K_d$) and Yield Coefficient ($Y$) of 0.0028 and 0.5083 respectively were obtained for this study as seen in Figure 5. Kinetic parameters vary for different industrial wastewater based on the nature of raw materials processed and the nature of wastewater effluent. Table 2 shows a fit of the obtained kinetic coefficients in Equation (4), (5), (9), (10) and (15) for substrate utilization rate, maximum bacterial growth rate, bacterial growth rate, microbial death rate and net biomass production rate respectively.

| Table 2: Parameters for Substrate Utilizations and Biomass Growth Prediction |
|-----------------------------------|------------------|------------------|
| Parameter                        | Equation         | Predictive Equation |
| 1 Substrate utilization rate      | $r_{su} = \frac{kSX}{K_s + S}$ | $r_{su} = \frac{4.45X}{275 + S}$ |
| 2 Maximum bacterial growth rate   | $\mu_{max}=kY$   | $u_{max}=4.4 \times 0.5083= 2.236$ |
3.3 Kinetic parameters obtained and their significance

3.3.1 Maximum Rate of Substrate Utilization (K) 
K represents the maximum rate of substrate utilization per unit mass of microorganisms. K was obtained as 4.4 day\(^{-1}\) in the present study. Maximum substrate utilization rate has significance in the design of the volume of reactor for biological system, the greater the value of K, the smaller will be the size of the reactor (Benefield and Randall, 1980).

The value obtained in this study falls within the general range of 2-10 day\(^{-1}\) for wastewater treatment reported by Tchobanoglous, et al. (2003). A value as low as 0.216 day\(^{-1}\) was reported for fertilizer industry wastewater by Gupta and Sharma (1996), while Haydar and Aziz (2009) obtained 3.125 day\(^{-1}\) for tannery wastewater. Ambreen, et al. (2013) reported 4.46 day\(^{-1}\) for dairy wastewater, which is close to that obtained in this work. These variations may be attributed to the characteristics nature of the various wastewaters studied. Industrial wastewater varies in nature depending on an industry manufacturing processes (Sharma, 2011). In addition, bio-kinetics depends on the actual environment and the biological metabolic activities in a system (Prakash and Sockan, 2014). Petroleum refinery wastewater often contains oil, ammonia, sulfides, chlorides, mercaptans, phenols and other hydrocarbons (Jou and Huang, 2003).

3.3.2 Half Saturation Constant (K\(_s\))
The substrate concentration at which specific substrate utilization rate is half of maximum substrate utilization rate is called half saturation constant, it is analogous to the half velocity constant (V\(_{max}\)) in the Michealis-Menten model. K\(_s\) was obtained as 275 mg/L in the present study which is large compare to 165.8 mg/L obtained by Andress, et al., (2011) for an onsite study of petroleum refinery wastewater treatment plant located in the Midwestern United State, to establish site-specific bio-kinetic constants for the existing wastewater treatment facility. Zhong, et al. (2003) reported 154 mg/L for petrochemicals wastewater.

As reported by Ambreen et al., (2013) large value of K\(_s\) shows that the maximum specific yield of bacteria occurs at high substrate concentration. Therefore, the relatively high value obtained in the present study is an

<table>
<thead>
<tr>
<th>(S/N)</th>
<th>Author</th>
<th>Wastewater</th>
<th>(K) (day(^{-1}))</th>
<th>(K_s) (mg/l)</th>
<th>(Y) mgVSS/mgCOD</th>
<th>(K_d) (day(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>This work</td>
<td>Petroleum</td>
<td>4.4</td>
<td>275</td>
<td>0.5083 mgVSS/mgBOD</td>
<td>0.003</td>
</tr>
<tr>
<td>2</td>
<td>Ambreen, et al.(2013)</td>
<td>Dairy</td>
<td>4.46</td>
<td>534</td>
<td>0.714</td>
<td>0.038</td>
</tr>
<tr>
<td>3</td>
<td>Zhong, et al. (2003)</td>
<td>Petrochemicals</td>
<td>0.185 h(^{-1})</td>
<td>154</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Andress, et al., (2011)</td>
<td>Petroleum</td>
<td>0.274</td>
<td>165.8</td>
<td>0.424</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>Mardani, et al. (2011)</td>
<td>Municipal</td>
<td>0.95-0.98</td>
<td>52-71</td>
<td>0.48-0.8</td>
<td>0.0189-0.026</td>
</tr>
<tr>
<td>6</td>
<td>Haydar and Aziz (2009)</td>
<td>Tannery</td>
<td>3.125</td>
<td>488</td>
<td>0.64 mgVSS/mgBOD</td>
<td>0.035</td>
</tr>
<tr>
<td>7</td>
<td>Prakash and Sockan (2014)</td>
<td>Tannery</td>
<td>1.66</td>
<td>1132</td>
<td>0.22</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3: Obtained Kinetic Coefficients and Previous Works
indication that the process bacteria yield occurred at higher substrate concentration. $K_s$ has no direct application in the process design, its significance is of theoretical nature and gives an idea about change in specific growth rate of bacteria with more a change in the concentration of growth limiting substrate (Benefield and Randall, 1980).

3.3.3 Biomass Yield (Y)

Yield Coefficient or Biomass Yield is the mass of cells produced per unit of substrate utilized which may be measured as mgVSS/mgCOD, it may also be described as how biomass is produced against substrate utilized. A value of 0.5083 mgVSS/mgBOD was obtained in this study, which is within the typical range of 0.4-0.8 reported by Sperling (2007). Previously, Andress, et al., (2011) obtained 0.424 mgVSS/mg COD for an onsite study for an existing petroleum refinery wastewater treatment plant. Yield coefficient of 0.714 mgVSS/mgBOD was reported by Ambreen et al. (2013). Haydar and Aziz (2009) reported 0.64 for tannery wastewater treatment in activated sludge process.

These differences may be attributed to the variations in the wastewater compositions. According to Tchobanoglous, et al (2003) bio kinetic coefficients depend on the kind of wastewater and its contents. The significance of Y in process design is that it gives an estimate of the sludge produced as a result of wastewater treatment. The greater the value of Y, the greater will be the amount of sludge, and the size of sludge handling facility. Preliminary cost estimates for sludge handling can be found out once the size is known (Ambreen, et al., 2013).

3.3.4 Endogenous Decay Coefficient ($K_d$)

Endogenous decay coefficient represents the fraction of the cells oxidized by endogenous respiration per unit of time. An endogenous decay coefficient of 0.003 d$^{-1}$ was obtained in this study. The range of $K_d$ generally for wastewater treatment is 0.06-0.100 d$^{-1}$ (Sperling, 2007). Andress, et al., (2011) obtained 0.01 d$^{-1}$ in another study of petroleum refinery wastewater. Haydar and Aziz (2009) reported 0.035 d$^{-1}$ for tannery wastewater while Ambreen et al (2013) also reported another close value of 0.038 d$^{-1}$ for dairy industry wastewater.

The very low value of $K_d$ obtained in this study is an indication of low bacterial decay rate, on the other hand the yield coefficient, Y was observed to be relatively high above the general minimum of 0.3 reported by Tchobanoglous, et al. (2003).The higher value of yield coefficient (Y) and lower value of organism decay ($K_d$) obtained shows that there is extremely higher production of excess sludge in the process. This implies that optimum sludge removal at frequent intervals has to be designed and sludge disposal mechanism has to be developed (Ashwin and Ramakrishniah, 2014). $K_d$ has reasonable significance in the design of activated sludge process as it is used in the evaluation of net sludge production in activated sludge process. According to Benefield and Randall (1980), it can be used to fine-tune the size of sludge handling facilities resulting in some economic benefits in the cost reduction.

4. CONCLUSION

Petroleum refinery wastewater biodegradation in an activated sludge process gave the following kinetic coefficients: Maximum Substrate Utilization Rate=4.4 day$^{-1}$, Half Saturation Constant=275 mg/L, Yield Coefficient=0.5083 mgVSS/mgBOD and Endogenous Decay Constant=0.003 day$^{-1}$. These kinetic coefficients are useful as predictive and diagnostic tool for further design and control of activated sludge process for optimal process performance.

REFERENCES


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